

UDC 666.76

INCONGRUENT EVAPORATION OF CERAMIC-MOLD OXIDES AT HIGH TEMPERATURES AND LOW PRESSURES

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Translated from *Steklo i Keramika*, No. 7, pp. 19–21, July, 2011.

The thermal dissociation of silicon and iron oxides, which are present in corundum-sillimanite ceramic molds when pouring heat-temperature alloys at high temperatures, is studied. Theoretical investigations determined that the silicon present in a ceramic mold is unstable with respect to thermal dissociation at 1873 K. It was found that iron oxide will undergo intense evaporation in the melting zone at low pressures 0.65–1.33 Pa. This phenomenon increases the chemical activity of the ceramic mold in the zone of contact with heat-resistant alloys and is a source of contamination of the cast surface.

Key words: corundum-sillimanite ceramic mold, incongruent evaporation of silicon and iron oxides.

In investment casting of high alloys the ceramic mold largely determines the possibility of nonmetallic endo- and exogenic inclusions appearing on the cast surface of and inside a metal. In the case of cast blades in aircraft engines some surface defects are eliminated by mechanical means, but small internal inclusions revealed by x-ray diffraction are the ones responsible for the final rejection of castings. These castings are obtained by pouring alloys containing chemically active elements, such as aluminum, titanium, and chromium, in substantial quantities at temperature 1823–1873 K and low pressure in the casting zone. For this reason the behavior of the components of a ceramic mold under such conditions is a very topical problem.

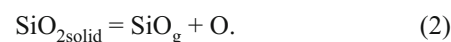
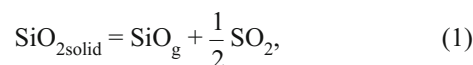
For this category of castings a ceramic mold is obtained by investment casting using as the refractory fill a suspension of a concentrate of disthene-sillimanite powder (CDSP), whose composition is $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, and an organosilicon binder, whose burn-out forms crystalline silica.

A qualitative, post-kilning x-ray phase analysis performed with a DRON-3 analyzer of the surface of corundum-sillimanite molds showed that, aside from the main phases, magnesium and calcium inclusions are dispersed at the edges of the surface while titanium and iron inclusions are present in a concentrated form. These elements enter as oxides into the composition of disthene-sillimanite, and according to TU 48-4-307-74 their concentration does not exceed 1.5, 0.8, 0.4 and 0.2% for TiO_2 , FeO , MgO , and CaO , respectively.

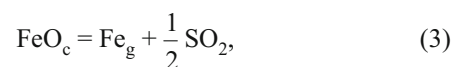
The thermal dissociation (TD) of the oxides that are unstable at high temperatures can determine the intensity of the

metal–mold interaction. The criteria for the instability of the oxides with respect to TD in vacuum are the volatility, expressed in terms of the total vapor pressure, and the rate of evaporation of the oxides, determined according to the Hertz–Langmuir equation as a function of the oxygen partial pressure.

It is shown in [1, 2] that, thermodynamically, the most advantageous process is gaseous TD (incongruent evaporation) of silica in reactions accompanied by a minimal reaction energy per mole of gaseous products at standard conditions (298 K). For silica these reactions have the form



Incongruent evaporation of iron monoxide can be represented by the reactions



The computed partial pressures of the gas-phase components above silica and iron monoxide [1, 3] show that the main gas-phase components at 1000–3000 K are SiO and O_2 , Fe and O_2 , respectively.

The total pressure $\Sigma p(\text{SiO}_2)$ and the silicon monoxide and molecular oxygen partial pressures $p(\text{SiO})$ and $p(\text{O}_2)$

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TABLE 1. Vapor Pressure and Evaporation Rates of Oxides at Different Temperatures

| Index | Index values at mold temperatures | | |
|--|-----------------------------------|--------------------------|-------------------------|
| | 1643 K | 1773 K | 1873 K |
| Vapor pressure, 10^{-3} Pa: | | | |
| $\Sigma p(\text{SiO}_2)$ | 1.52 | 26.50 | 181.1 |
| $p(\text{SiO})$ | 0.91 | 15.71 | 106.3 |
| $p(\text{O}_2)$ | 0.23 | 4.03 | 27.7 |
| Vapor pressure, 10^{-3} Pa: | | | |
| $\Sigma p(\text{FeO})$ | 2.59 | 25.10 | 113.5 |
| $p(\text{Fe})$ | 1.55 | 14.82 | 64.6 |
| $p(\text{O}_2)$ | 0.94 | 7.08 | 31.1 |
| Evaporation rate J , $\text{kg}/(\text{m}^2 \cdot \text{sec})$, oxides: | | | |
| $J(\text{SiO}_2)$ for $p(\text{O}_2)$: | | | |
| 10^5 Pa | 3.15×10^{-10} | 469.21×10^{-10} | 693.0×10^{-10} |
| 0.26 Pa | 1.92×10^{-6} | 10.12×10^{-6} | 231.0×10^{-6} |
| 0.13 Pa | 7.15×10^{-6} | 148.13×10^{-6} | 805.0×10^{-6} |
| $J(\text{FeO}_2)$ for $p(\text{O}_2)$: | | | |
| 10^5 Pa | 4.66×10^{-8} | 47.6×10^{-8} | 689.2×10^{-8} |
| 0.26 Pa | 0.66×10^{-4} | 6.2×10^{-4} | 152.0×10^{-4} |
| 0.13 Pa | 26.11×10^{-4} | 251.1×10^{-4} | 7140.7×10^{-4} |

above silicon dioxide were determined from the following equations [3]:

$$\log \Sigma p(\text{SiO}_2) = -25,597/T + 8.99; \quad (5)$$

$$\log p(\text{SiO}) = -27,505/T + 8.71; \quad (6)$$

$$\log p(\text{O}_2) = -27,809/T + 8.29. \quad (7)$$

In Eqs. (5)–(7) the pressures are expressed in atmospheres.

The evaporation rate of the oxides, expressed in terms of the maximum flux of the components in terms of their TD, was found using the Hertz–Langmuir equation:

$$J_{i\max} = (2\pi M_i RT)^{-1/2} p_i, \quad (8)$$

where $J_{i\max}$ is the maximum flux of the i th component leaving the surface of the reacting substance, in $\text{moles}/(\text{cm}^2 \cdot \text{sec})$; M_i is the molecular mass of the i th component; R is the universal gas constant expressed in $\text{cm}^3 \cdot \text{atm}/(\text{K} \cdot \text{mole})$; and, p_i is the equilibrium partial pressure of the i th component above the surface of the substance, in atm.

In Eq. (8), the silicon monoxide partial pressure $p(\text{SiO})$ was expressed in terms of the oxygen partial pressure $p(\text{O}_2)$ in conformance to the reactions (1) and (2). Assuming the activity of the condensed phase of SiO_2 to be 1 we can write

$$p(\text{SiO}) = \exp[-\Delta G^0(T)/RT] \{p(\text{O}_2)\}^{-1/2}, \quad (9)$$

where $\Delta G^0(T)$ is the standard change of the Gibbs reaction energy of incongruent evaporation.

We now substitute the value of $p(\text{SiO})$ into the Hertz–Langmuir equation and at the same time express the SiO flux in grams of the silica flux, taking account of the fact that one mole of SiO is obtained from one mole of SiO_2 . Next, we multiply the SiO flux by the silica molecular mass and obtain

$$J(\text{SiO}_2) = [1596 \times 10^5 / T^{1/2}] \times M(\text{SiO}_2) \times \{\exp[-\Delta G^0(T)/RT] / [M(\text{SiO})]^{1/2}\} \times [10 \times p(\text{O}_2)]^{-1/2}, \quad (10)$$

where $J(\text{SiO}_2)$ is the minimal SiO_2 flux expressed in terms of the silicon oxide mass, in $\text{g}/(\text{cm}^2 \cdot \text{h})$; $p(\text{O}_2)$ is the oxygen partial pressure, in MPa; and, $M(\text{SiO}_2)$ and $M(\text{SiO})$ are the molecular masses of the oxides.

This equation was also used to calculate the maximum flux during incongruent evaporation of FeO . The values of the partial pressures of the components with gaseous dissociation were taken from [3]. The computational results obtained for the partial vapor pressures and evaporation rates of silica and iron monoxide in the temperature interval 1643–1873 K with oxygen partial pressures 0.13, 0.26, and 10^5 Pa are presented in Table 1.

The data obtained show that the stability of binder silica with respect to TD in vacuum is low. As temperature increases to 1873 K, the total pressure of SiO and O_2 increases to 0.18 Pa, i.e., less than an order of magnitude lower than the residual pressure (1.33–0.65 Pa), produced in vacuum melting-casting facilities. For this reason, when heat-temperature alloys are poured into corundum-sillimanite molds the silicon dioxide in the binder can undergo partial sublimation.

The vapor pressure above iron oxide at 1873 K ($p = 1.135$ Pa) differs little from the residual pressure in the casting zone $p_{\text{res}} = 1.33$ Pa, and for fusion at $p_{\text{res}} = 0.65$ Pa the vapor pressure is more than a factor of 1.75 higher. This gives rise to intense sublimation of FeO under casting conditions.

Calculations of the evaporation rates of these oxides have shown that as temperature increases from 1773 to 1873 K their values increase more than 14-fold. For industrial vacuum $p(\text{O}_2) = 0.26$ – 0.13 Pa the SiO_2 and FeO evaporation rates increase sharply and reach, respectively, $(2.31$ – $80.5) \times 10^{-4}$ and $(1.52$ – $71.4) \times 10^{-2}$ $\text{kg}/(\text{m}^2 \cdot \text{sec})$. It should be noted that the FeO evaporation rate in this case is 64–85 times higher than that of SiO_2 .

According to the data of [3], the vapor pressure above calcium, titanium, and aluminum oxides in the experimental temperature interval is much lower than above silica; this confirms that they are highly stable with respect to TD in vacuum.

In summary, the calculations performed here show that during the casting of an alloy the surface temperature of the

mold increases sharply and conditions for sublimation of silicon and especially iron oxides together with their simultaneous dissociation into components, whose chemical activity is higher than that of the initial oxides with respect to the elements of the alloy, are created. At the same time, nonmetallic surface inclusions and sub-skin bubbles form in the casting; some of them are larger than the tolerances for mechanical working of the surface of the cast article. During casting in a continuous melting – casting furnace, where the temperature of a ceramic mold increases gradually, the residence time of the mold in the high-temperature zones increases. To de-

crease the chemical activity of the ceramic mold its content of silicon and iron oxides must be reduced.

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